Dipterexと五硫化リンとの反応

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The Reaction of Dipterex with Phosphorus Pentasulfide. Yoshihiko NISHIZAWA and Masataka NAKAGAWA (Sumitomo Chem. Co. Ltd., Osaka) Received Sept. 1, 1960. *Botyu-Kagaku*, **25**, 132, 1960. (in English)

24. Dipterex と五硫化リンとの反応

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35. 9. 1. 受理

有機リン殺虫剤の研究途上において 著者等は Dipterex と 五硫化リンの反応を試みた結果，本反応の反応主生成物は thiono-Dipterex $(CH_3O)_2P(S)CH(OH)CCl_3$ 或いは thiol-Dipterex $(CH_3O)_2P(O)CH(SH)CCl_3$ ではなく 0, 0-bis-1-(0, 0-dimethyl phosphonyl)-2, 2, 2-trichloroethyl phosphorodithioate*1) $[(CH_3O)_2P(O)CH(CCl_3)O]_2P(S)SH$(III) であることを見出した．

0,0-Dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphonate (I) which is developed by Farbenfabriken Bayer A. G.[1] is the low toxic organophosphorus insecticide and is well known as "Dipterex"

All of the reported or commercial organophosphorus insecticides have the phosphoroate forms $(RO)_2P(O)OR'$, phosphorothioate forms $(RO)_2P(S)OR'$ or phosphorodithioate forms $(RO)_2P(S)SR'$, with exception of Dipterex which has phosphonate form $(RO)_2P(O)R'$. Accordingly, many investigations have been reported on the correlations between the chemical structure and the biological activity[1~6] of Dipterex. In spite of these efforts, it is not yet cleared whether Dipterex reacts with the enzyme as the phosphonate form or as the other form which is changed in *vivo*.

One of the causes which complicate these studies may be that Dipterex is easily dehydrochlorinated to 0, 0-dimethyl-0-2, 2-dichlorovinyl phosphoroate (DDVP) (II) by enzymatic or nonenzymatic reactions and DDVP has also high activity towards the acetylcholinesterase.

$$\underset{\text{(I)}}{(CH_3O)_2P(O)CHCCl_3}\ \underset{OH}{}\ \xrightarrow{-HCl}\ \underset{\text{(II)}}{(CH_3O)_2P(O)OCH=CCl_2}$$

It seems to be the most leading hypothesis at present that Dipterex may probably convert to DDVP *in vivo* and DDVP may attack the acetylcholinesterase.

In order to confirm the above hypothesis, Casida[4] prepared the Dipterex derivatives which are hard to convert into DDVP and tested their activities. For instance, the hydroxyl radical of Dipterex was protected by acetyl radical for preventing the rearrangement reaction by intercepting the supply of the hydrogen atom in dehydrochlorination reaction. But, this attempt was not successful because the acetyl derivative was decomposed quickly *in vivo*.

The authors considered from the above reports that it might be possible to get on some tracks explaining the action mechanism of Dipterex, if the hydroxyl radical of Dipterex was covered with the phosphorothioate radical. Consequently, the reaction of Dipterex with phosphorus pentasulfide was attempted and the structure of the product was determined.

When a solution of four moles ratio of Dipterex and one mole ratio of phosphorus pentasulfide suspending in toluene was heated, hydrogen sulfide gas evolved and phosphorus pentasulfide dissolved in toluene during the reaction. After the evaporation of toluene, the pale yellow viscous oil (III) was obtained. This viscous oil (III) had the characteristic odour of phosphorodithioate and showed to be acidic in aqueous alcoholic solution and was soluble in aqueous alkaline solution, while Dipterex is neutral in the same condition. Moreover, the viscous oil (III) showed the violet colour reaction with cobalt sulfate and reacted with pyridine to produce the more viscous syrup which is soluble in alcohol, acetone and water, but insoluble in benzene and ether. It was shown by paper chromatography that the viscous oil (III) consisted mainly of phosphorodithioate and of a trace of

*1) The phosphorus compounds in this paper were named according to the Drake Committee's Report (*Chem. Eng. News*, 30, 4515, 1952)

five phosphorus compounds, one of which coincided with Dipterex in Rf. The main product was purified by column chromatography and the barium salt was prepared. By the microanalytical data of barium salt the main product of this reaction was found to be 0,0-bis-1-(0,0-dimethyl phosphonyl)-2,2,2-trichloroethyl phosphorodithioate. Consequently, it was considered that the reaction proceeded according to the following scheme:

The compound (III) was less toxic to the mice

$$4(CH_3O)_2P(O)\underset{\underset{OH}{|}}{C}HCCl_3 + P_2S_5 \longrightarrow 2[(CH_3O)_2P(O)\underset{\underset{CCl_3}{|}}{C}HO]_2P(S)SH + H_2S$$

(I) (III)

than Dipterex. The compounds (III), when sprayed directly to the insects, was less active than Dipterex. However, when the product was contacted with the insects after passing through the plants, it showed the same activity as that of Dipterex.

This difference on the activity seems to be very interesting. The activities towards the insects and the acetylcholinesterase of brain of housefly will be reported in other papers.

Experimental

A solution suspending 37g(M/7) of Dipterex and 8.9g (M/28) of phosphorus pentasulfide in 80 ml of toluene was heated at 80° for 2 hours under stirring.

The phosphorus pentasulfide became to dissolve in toluene with evolution of hydrogen sulfide, which was led into the aqueous solution of the mercuric chloride to give 2.1g of mercuric sulfide. After the phosphorus pentasulfide dissolved completely, the reaction mixture was continued to stirr for one hour at the same temperature. Toluene was distilled off and 42g of the pale yellow viscous oil was obtained. This viscous oil had the characteristic odour of phosphorodithioate and showed to be acidic in aqueous alcoholic solution and soluble in aqueous alkaline solution. Moreover, the viscous oil showed the violet color reaction with cobalt sulfate, reacted with pyridine to give the more viscous syrup which is soluble in alcohol, aceton and water, but insoluble in benzene and ether. By the paper chromatography using butanol, acetic acid and water mixture as solvent (Rf. 0.64 at 25°) and the solution of iodine and chloroplatinic acid as color former, it was clarified that the viscous oil contained one phosphorodithioate. On the other hand, it was shown that the viscous oil contained a trace of five phosphorus compounds by using ammonium molybdate as color former. It was determined that one of them was Dipterex in Rf. The pure compound was obtained by passing through the alumina column (3×20cm), using toluene as solvent. Anything could not be detected in the pure compound except one phosphorodithioate.

Into the solution of 27.3g(M/30) of the pure compound in 100 ml of 1-N aqueous solution of barium hydroxide, carbon dioxide was passed to remove the excess barium hydroxide. After the solution was filterd off and concentrated *in vacuo*, 16.8g of white barium salt was obtained and recrystallized from ethanol.

Anal. Calcd. for

$C_8H_{14}O_8Cl_6P_3S_2{}^1/_2Ba$;	P, 13.7;	S, 9.5
Found	P, 13.8;	S, 9.3

Summary

The reaction of Dipterex with phosphorus pentasulfide produced neither thiono-Dipterex $(CH_3O)_2P(S)CH(OH)CCl_3$ nor thiol-Dipterex $(CH_3O)_2P(O)CH(SH)CCl_3$, but mainly 0,0-bis-1-(0,0-dimethyl phosphonyl)-2,2,2-trichloroethyl phosphorodithioate $[(CH_3O)_2P(O)C(H)(CCl_3)O]_2P(S)SH$ (III).

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